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Homogeneous Organolanthanide Catalysts for the Selective Polymerization of Styrene without Aluminium Cocatalysts

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Anionic or neutral allylic samarium or neodymium species catalyse the polymerization of styrene (catalyst/styrene ratio = 1:1000) without addition of a cocatalyst. Random syndiotactic-rich material is obtained from tetra-allyl-lanthanides, whereas neutral trisallyl-lanthanides or anionic *ansa*-bis(cyclopentadienyl)bisallyl-lanthanides afford isotactic-rich polystyrene. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Lanthanide complexes have been widely investigated as catalysts for diene polymerization, some of them giving high yields of *cis*-polybutadiene.[1–7] All these experiments were carried out in the presence of organoaluminium cocatalysts. On the other hand, styrene polymerization catalysed by rare-earth complexes has been much less studied. All the systems tested contain organoaluminium cocatalysts[2,3,7–10] or cationic Ziegler–Natta-type complexes.[9,10] The polystyrenes obtained are generally atactic, however an isotactic material was obtained from a neodymium phosphonate/tris(isobutyl)aluminium system, after water addition,[11,12] whereas a syndiotactic-rich polymer was synthesized from neodymium trisnaphthalenide/tris(isobutyl)aluminium after addition of water.[13] In previous papers, we reported the high-yield stereospecific *trans* polymerization of isoprene using rare-earth organometallic complexes as catalysts without organoaluminium cocatalysts.[14,15] This paper reports on the selective syndiotactic or isotactic polymerization of styrene using single-site anionic and neutral allyl-lanthanide catalysts.

EXPERIMENTAL

Reagents and standards

All operations were performed under argon using standard vacuum techniques or in an atmosphere of purified nitrogen in a Jacomex glovebox (>2 ppm O_2). Solvents were distilled from appropriate drying agents, stored over sodium/benzophenone and vacuum-transferred to reaction vessels. Styrene (99%) was dried over molecular sieves and stored in darkness at −18 °C under argon. It was distilled twice just before use to eliminate the stabilizer. $(C_3H_5)Li(dioxane)$ **(1)**,[16] $[Sm(C_3H_5)_4]Li(dioxane)_{1.5}$ **(2)**,[17] $[Nd(C_3H_5)_4]Li(dioxane)_{1.5}$ **(3)**,[16] $Nd(C_3H_5)_3(dioxane)_{1.5}$ **(4)**, $[(C_5H_4CMe_2CMe_2C_5H_4)Sm(C_3H_5)_2]$ Li(dimethoxyethane) **(5)**,[15] $NdCl_3(THF)_3$[19] and [18]$(C_5H_4CMe_2CMe_2C_5H_4)(MgCl)_2(THF)_4$[20] were synthesized following published methods.

Apparatus

Gel permeation chromatography analyses were run on a Spectra Physics Chromatograph using UV and refractive-index detectors connected in series. Calibration was carried out with PL Lab polystyrene standards (Easical PS-1, M_w range (580–8.5) $\times 10^6$). Each measurement was performed at 25 °C in THF with a 1 ml min^{-1} flow rate. NMR spectra were recorded at room temperature on a Bruker AC 500 spectrometer operating at 500 MHz for ^{1}H and 128 MHz for ^{13}C. Chemicals shifts were expressed in parts per million (ppm) downfield

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from external TMS (^1H and ^{13}C). NMR samples were prepared by dissolving the polystyrene in $CDCl_3$ and heating for 5 min at 50 °C to increase the solubility. Differential scanning calorimetric (DSC) measurements were carried out on a 2920 modulated DSC TA Instruments calorimeter.

Synthetic procedures

$[Me_4C_2Cp_2Nd(C_3H_5)_2]Li(dioxane)$ (6)

Onto a mixture of $NdCl_3(THF)_3$ (1.09 g, 2.34×10^{-3} mol) and $(Me_4C_2Cp_2)(MgCl)_2(THF)_4$ (1.54 g, 2.34×10^{-3} mol) as solids, toluene (40 ml) was condensed at −80 °C and allowed to warm back to room temperature within 10 min. The resulting suspension was stirred for two days. Salts were separated by filtration and $(C_3H_5)Li(dioxane)$ (0.7 g, 5.12×10^{-3} mol) was added to the resulting reddish-green solution. The mixture turned apple green, and after removal of the solvent under vacuum pressure, a green oil with red glints was obtained. This oil was dissolved in ether (20–30 ml) and stirred at room temperature for some hours until the salts precipitated. After filtration, evaporation of the solvent afforded **6** as a green solid in *ca* 60% yield. This compound contained a small amount (*ca* 2%) of magnesium salts, detected by elemental analysis.

$(Me_4C_2Cp_2)Nd(C_3H_5)$ (7)

The complex **6** (126 mg) was dissolved in 10 ml of dioxane and 0.4 ml of a 1 M solution of BEt_3 in hexane was added slowly at room temperature. After 4 h, the colourless allyltriethylborate was eliminated by filtration and the dichroic reddish-green solution concentrated. No crystallization occurred after pentane addition; after evaporation of the solvents, the crude material was extracted with 5 ml of benzene, leaving a bright green powder. Yield: 35%.

General polymerization procedure

The polymerization flask was dried by flaming under vacuum and flushed with argon. The procedure was repeated three times. The catalyst (5 mg) was introduced into the flask in the glove box. Freshly distilled styrene was then added with a syringe and the reaction mixture was kept in a thermostatic bath for a given time. In some experiments a solvent [toluene or hexane (1 ml)] was added to the mixture. Depending on the activity of the catalyst, the solution could turn highly viscous. After the stirring was stopped, the reaction mixture was dissolved in the required volume (2–10 ml) of toluene and the solution was poured into 200 ml of ethanol. The precipitated polymer was washed with ethanol and dried under vacuum.

RESULTS AND DISCUSSION

Anionic compounds **1, 2, 3, 5** and **6** as well as neutral compound **4** were active towards the polymerization of styrene in a styrene/lanthanide molar ratio of 1000. In contrast with other reported systems, these catalysts did not need to be activated with a cocatalyst. These compounds showed important differences of activity, and mainly of stereoselectivity: **1** afforded atactic material; **2** and **3** gave a random syndiotactic-rich polymer; and **4, 5** and **6** gave isotactic-rich polystyrene.

The structural characteristics of the polystyrenes were established by ^{13}C-NMR spectroscopy. This method is used extensively to obtain detailed information on the microstructure of vinyl polymers. The signals of the methylene and the C-1 carbons of polystyrene have been assigned to reflecting configurational frequences.[21–25] The most important signal for determining stereoregularity was the phenyl C-1 carbon signal. For this reason the NMR spectra were studied especially in the range 140–150 ppm, in which two main peaks can be related unambiguously to the tacticity of polystyrene: 146.8 ppm for isotactic (*mmmm* pentad), and 145.7 ppm for syndiotactic (*rrrr* pentad), whereas a broad signal centred at 146.4 ppm was recorded in the same conditions for an atactic material. These values were recorded in $CDCl_3$ (77.43 ppm) at room temperature.

Styrene can be self-polymerized at high temperature. In order to assess the effect of heat on the polymerization, experiments were performed under the standard conditions, without a catalyst (Table 1). These experiments showed that the effect of thermal polymerization could be neglected.

Table 2 summarizes the results obtained with

Table 1 Thermal polymerization of styrene

Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-3}$
50	50	2	635
70	40	17	1000
110	5	77	340

Table 2 Polymerization of styrene with compounds **1–4**

Run	Catalyst	Temp. (°C)	Time	Solvent	Conversion (%)	$M_w \times 10^{-3}$ (Idp)[a]
1	**1**	20	5 min	None	100	800 (2.5)
2	**1**	50	30 min	Toluene	100	500 (2.5)
3	**2**	50	2 h 30 min	None	100	620 (2.8)
4	**3**	0	4 h	None	0	—
5	**3**	20	2 h 50 min	None	100	200 (3)
6	**3**	50	20 min	None	100	160 (4.7)
7	**3**	100	1 min	None	100	200 (3.5)
8	**3**	20	17 h	Toluene	97	170 (3.2)
9	**3**	50	1 h 30 min	Toluene	100	95 (4.5)
10	**3**	75	20 min	Toluene	100	280 (4.5)
11	**3**	15	50 h	Hexane	50	500 (–)
12	**4**	50	12 h	Toluene	8	8 (1.6)
13	**4**	50	12 h	None	60	18[b] (2.7)

[a] Idp,
[b] Soluble part in toluene

allyl-lithium **1** (runs 1, 2), tetra-allyl-samarium and-neodymium anions **2** and **3** (runs 3–11) and trisallylneodymium **4** (runs 12, 13). With tetra-allylsamarium (**2**) as catalyst, the reaction proceeded much more slowly than with the analogous neodymium compound **3**. This difference can be related to the size of the metal centres.

It is noteworthy that, with or without a solvent, the rate of polymerization was strongly dependent on the temperature and that polymerization occurred more rapidly with allyl-lithium than with lanthanide compounds **2** and **3**. ^{13}C NMR spectra in $CDCl_3$ for polystyrenes obtained with **2** and **3** showed a major peak at 145.7 ppm, corresponding to syndiotactic-rich random polymers (Fig. 1).

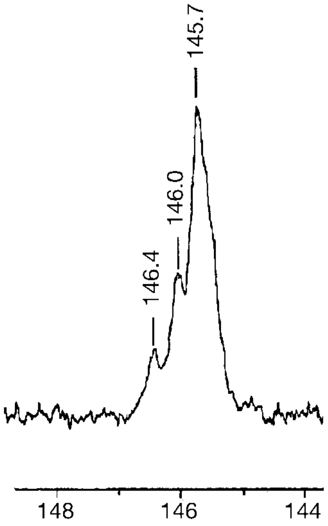

Figure 1 ^{13}C-NMR spectrum of syndiotactic-rich (run 6) polystyrene.

From trisallylneodymium **4**, in toluene solution (run 12), the polystyrene obtained in low yield was completely soluble in toluene but showed a major peak at 146.75 ppm, due to an isotactic-rich microstructure. When the reaction was carried without a solvent (run 13), the polystyrene obtained in 60% yield was only partially soluble in toluene. The insoluble material (*ca* 10%) was isolated. This polystyrene was sparingly soluble in $CDCl_3$ at 50 °C; the NMR spectrum showed well-defined signals at 146.75 ppm [aromatic C-1] 43.31 ppm (methine group) and 40.95 ppm (methylene group). Other aromatic signals at 146.1 and 145.7 ppm were of very low intensity (Fig. 2). This set of signals was in accordance with a quite pure isotactic polystyrene.

The DSC curves of this sample revealed a glass transition temperature (T_g) at 96 °C and a melting point (T_m) at 225 °C. The very sharp peak of the melting phase indicated significant crystallinity.

These results can be related to the behaviour of the catalyst in solution. The unsaturated allylneodymium complex **4** could easily coordinate styrene and afforded isotactic polymer in high yield (run 13). In the presence of aromatic solvents, competition between styrene and solvent led to a system of very low activity (run 12).

It is well known that allyl-lithium is a very efficient anionic initiator, inducing an atactic polymerization process. Catalysts **2** or **3**, in the

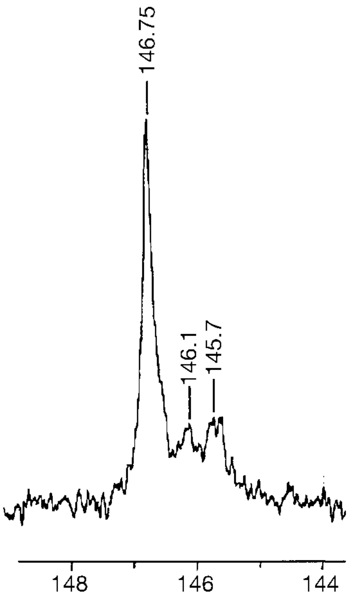

Figure 2 ^{13}C-NMR spectrum of isotactic-rich (run 13) polystyrene.

presence of coordinative species (solvents or monomers), can be regarded as being in equilibrium with a mixture of allyl-lithium and neutral trisallylneodymium[26] (Eqn [1]).

$$[(\text{allyl})_4\text{Ln}]\text{-Li} \longrightarrow (\text{allyl})_3\text{Ln} + (\text{allyl})\text{Li} \qquad [1]$$

Then, different catalytic processes could occur: from allyl-lithium, from neutral lanthanide or from anionic lanthanide. Nevertheless, the obtainment of a syndiotactic-rich material (runs 3–11) did not account for a preponderant participation of allyl-lithium and trisallylneodymium, independently acting in two simultaneous catalytic ways.

It seems plausible that coordination of the monomer occurred on the neutral trisallyl-lanthanide species, but allyl-lithium remaining in close proximity to the catalytic site might preferentially coordinate again to the lanthanide moiety. In that case, allyl-lithium did not act as a polymerization initiator, but essentially as a protecting group of the lanthanide active species.

The same experiments were performed using two other catalysts: the anionic species bisallyl-*ansa*-samarocene (**5**) and bisallyl-*ansa*-neodymocene (**6**). The latter was synthesized using the procedure previously described for **5**.[15] In these complexes, the bridge between the two cyclopentadienyl rings precluded the redistribution reactions (usually affording triscyclopentadienyl species) and enhanced the accessibility to the metal centre by opening the angle (Cp centroid)-metal-(Cp centroid). The results of these polymerization experiments are reported in Table 3.

The polymerization was faster with neodymium (runs 16–22) than with the samarium complex (run 15) and much slower than with allyl-lithium (runs 1 and 2). Polystyrenes so obtained were isotactic-rich, as indicated by the presence of a major peak at 146.7 ppm in the ^{13}C-NMR spectra. As reported above for **2** and **3**, the species **5** or **6**, in solution can be in equilibrium with the corresponding neutral lanthanide complex and allyl-lithium (Eqn [2]).

$$[(\textit{ansa}\text{-Cp}_2)\text{Ln}(\text{allyl})_2]\text{Li} \longrightarrow (\text{allyl})\text{Li} + (\textit{ansa}\text{-Cp}_2)\text{Ln}(\text{allyl}) \qquad [2]$$

The long reaction time, one day or more instead of a few minutes, suggested the absence of a noticeable participation of allyl-lithium and the intervention of a lanthanide organometallic moiety. Consequently, a sample of monoallylneodymium compound **7** was prepared, according to the method used to obtain **4** and **3**. This compound was found

Table 3 Polymerization of styrene with *ansa* compounds **5, 6** and **7**

Run	Catalyst	Temp. (°C)	Time	Solvent	Conversion (%)	$M_W \times 10^{-3}$ (Idp)
14	**5**	50	50 h	None	30	—
15	**6**	20	26 h	None	2	—
16	**6**	20	67 h	None	7	55
17	**6**	50	6 h	None	60	96 (1.6)
18	**6**	75	1 h 40 min	None	86	90 (1.34)
19	**6**	100	35 min	None	98	55 (2.1)
20	**6**	50	25 h	Toluene	100	110 (3.1)
21	**6**	100	7 h	Toluene	100	26 (3.2)
22	**6**	50	17 h	Hexane	100	16 (3)
23	**7**	50	48 h	None	3	—

to be inactive (run 23), as was also found to be the case for a related complex $[(C_5H_4tBu)_2Sm(allyl)]_n$; the lack of reactivity has been attributed to the strongly associated nature of this compound.[9]

The activity observed for complexes **5** and **6** tends to signify that a neutral active *ansa*-bis(cyclopentadienyl)lanthanide–allyl complex ought to be obtained *in situ* by the dissociation of a protective group, this group remaining in close proximity to the catalytic site to prevent the formation of strongly associated inactive complexes.

CONCLUSION

In conclusion, allylic lanthanide complexes act as single-site catalysts for the polymerization of styrene. The control of tacticity can be related to the structure of the catalysts. It is difficult to propose any interpretation or comment concerning the behaviour of the neutral compound **3** giving isotactic-rich material, because the nature (monomeric or associated) of this complex in solution is not clearly established. On the other hand, the behaviour of anionic complexes **2**, **3** and **5**, **6** can be interpreted. These complexes have been previously used as isoprene polymerization catalysts. The observed difference in stereoselectivity was tentatively related to the number of available coordination sites (two for **2** or **3**; one for **5** or **6**). The stereocontrol of styrene polymerization might be controlled by the same factors.

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